

SPECTRAL RESPONSE BEHAVIOUR OF PHOTOETCHED CdS ELECTRODES

Y RAMPRAKASH, V SUBRAMANIAN, R KRISHNAKUMAR and A S LAKSHMANAN

Central Electrochemical Research Institute, Karaikudi-623 006, INDIA

[Received: 1988 January; Accepted: 1988 February]

Photoelectrochemical studies in 1M NaOH-1M Na₂S-1M S on chemically etched and photoetched surfaces of single crystal CdS electrode have been carried out. The current-voltage characteristics at 120 mW cm⁻² tungsten-halogen illumination showed $V_{oc} = 265\text{mV}$, $J_{sc} = 52.08\text{ }\mu\text{A cm}^{-2}$ and $ff = 0.45$ for the photoetched surface. The spectral response curve depicting the variation of absolute quantum efficiency with wavelength of incident radiation showed a maximum value of 2.26×10^{-2} at a wavelength of 510nm. The results are compared with those obtained on a chemically etched surface.

Key words:- Photoetching, chemical etching

INTRODUCTION

Photoelectrochemical (PEC) cells convert light energy into electrical power or chemical energy. The chemical energy so generated can be in the form of fuels like hydrogen, methane, etc. In these cells, the surface of the semiconductor is always in contact with the electrolyte and hence is a source of various defects which inhibit the free passage of charge carriers across the interface. At these defects, the majority carriers get trapped and recombine with the minority carriers and this process results in a decrease in the quantum efficiency which is defined as the number of electron-hole pairs collected per incident photon.

Semiconductors used in solid state photovoltaic and photoelectrochemical devices are usually given a chemical etch in a suitable etchant to remove the surface damage which occurs during mechanical polishing. Electrolytic etching is used mainly for preferential etching (shaping) or polishing of semiconductors. However, removal of surface defects, the presence of which is detrimental to the performance of the semiconductor is not accomplished by this method. Photoelectrochemical etching or photoetching, in this context, has proved to be a useful technique and ensures removal of surface defects and thereby to improve the state of the semiconductor surface. Improvement in the performance of PEC cells based on CdS, CdSe, CdTe, CdSe₂Te_{1-x}CdIn₂Se₄, ZnSe and InSe which were subjected to photoetching treatment has been reported [1-6] in literature. In the present communication, we report our studies on the current-voltage behaviour and spectral response characteristics of a photoetched and a chemically etched CdS single crystal electrode.

EXPERIMENTAL

Small 1 cm dia single crystal discs of CdS ($\rho = 1.36 \times 10^3\text{ ohm cm}$, $n = 2.29 \times 10^{13}\text{ cm}^{-3}$) were used in the present investigations. The free electron concentration (n) has been calculated from the approximate relation $\rho = (ne\mu)^{-1}$ assuming $\mu = 200\text{ cm}^2\text{ V}^{-1}\text{ sec}^{-1}$ for electrons [7]. The crystals were mechanically polished using alumina powder. An ohmic contact was provided on the unpolished side by evaporated indium which was subsequently annealed at

100°C for 30 mt. Electrical contact to indium was given through a copper wire soldered to it. The portions of the electrode to be protected from electrolytic attack were coated with polystyrene except for a small area (approximately 0.72 cm²) which was to form the interface with the electrolyte.

The PEC cell was formed by dipping the CdS working electrode and the Pt counter electrode in an argon purged 1M NaOH-1M Na₂S-1M S redox. The argon bubbling was continued during the course of the experiment. The photoelectrode was illuminated with light from a tungsten-halogen lamp (Oriol 6432), incident intensity 120 mW cm⁻². The optical arrangement for the measurement of current and voltage under illumination was similar to the one described in our previous communication [6]. The spectral illumination scan was provided through a monochromator (Applied Photophysics) driven by a stepping motor. The entrance slit of the monochromator was illuminated by the tungsten-halogen lamp. The photocurrent across the current terminals of the Wenking Potential Control Amplifier (Model 72 L) was recorded on a Philips X-t recorder. The intensity of the monochromatic beam was calibrated against a Si photodiode of known spectral output.

Photoetching of the CdS surface

The polished face of the CdS electrode was chemically etched in conc. HCl for 30 sec. Photoetching was done in a 10 times diluted mixture of 97:3 HCl and HNO₃. During this process, the CdS working electrode was shorted to the Pt counter electrode and illuminated with white light at 120 mW cm⁻² for 30 sec.

RESULTS AND DISCUSSION

The diffuse reflectance spectrum for the CdS single crystal sample (polished surface exposed to the light beam) is shown in Fig.1. It can be seen that the reflectance is minimum upto a wavelength of 525 nm and thereafter rises steadily reaching a near saturation value of 28% at 600 nm. It may further be noted from the figure that the reflectance is only about 8.75% upto a wavelength of 525 nm. This shows that most of the light having energy greater than the bandgap of CdS ($E_g = 2.42\text{ eV}$) is absorbed. The transmission spectrum of 1M NaOH-1M Na₂S-1M S (Fig.2) shows only

34% transmittance at about 510 nm (2.43 eV), thus resulting in a considerable loss of light reaching the photoelectrode.

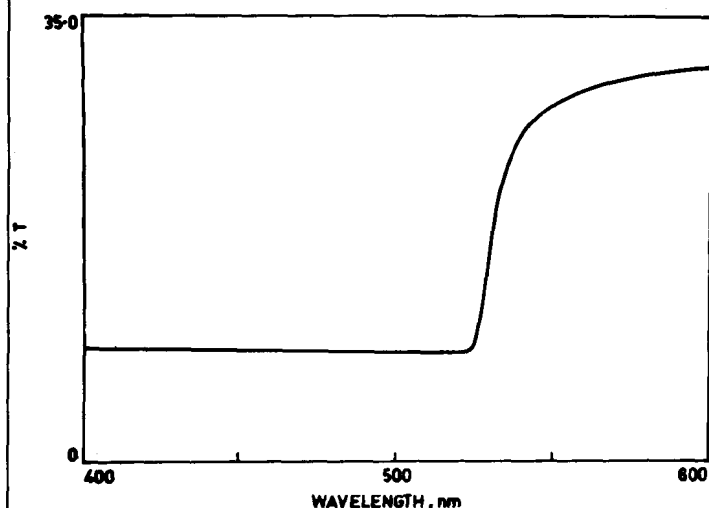


Fig. 1: Diffused reflectance spectrum of polished single crystal CdS (as obtained with a Hitachi UV-VIS-IR Spectrophotometer 3400)

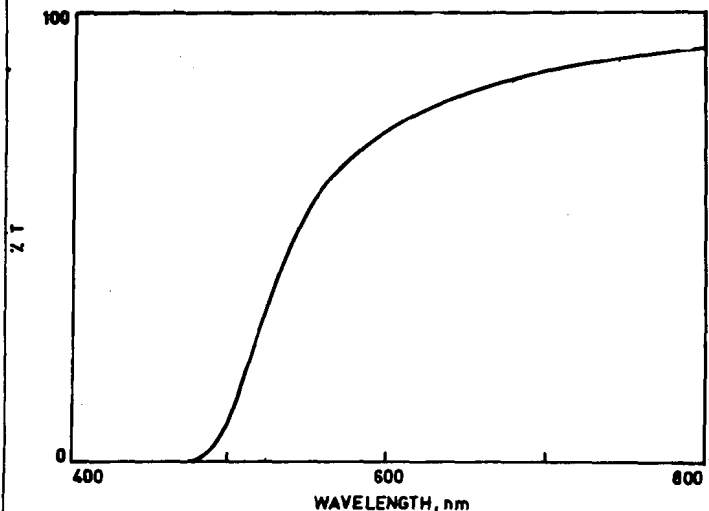


Fig. 2: Transmission spectrum of 1M NaOH-1M Na₂S-1M S

Fig. 3 shows the current-voltage curves under 120 mW cm⁻² illumination for a 0.72 cm² exposed area of the CdS surface. It can be seen that the chemically etched surface shows $V_{oc} = 227$ mV, $J_{sc} = 40.27 \mu A cm^{-2}$ and $ff = 0.36$. The beneficial effect of a short photoetching is evident from the improvement in the J-V characteristic which showed $V_{oc} = 265$ mV, $J_{sc} = 52.08 \mu A cm^{-2}$ and $ff = 0.45$. This improvement may be attributed to reduced reflection losses from the CdS surface and increased surface area on account of photoetching [3].

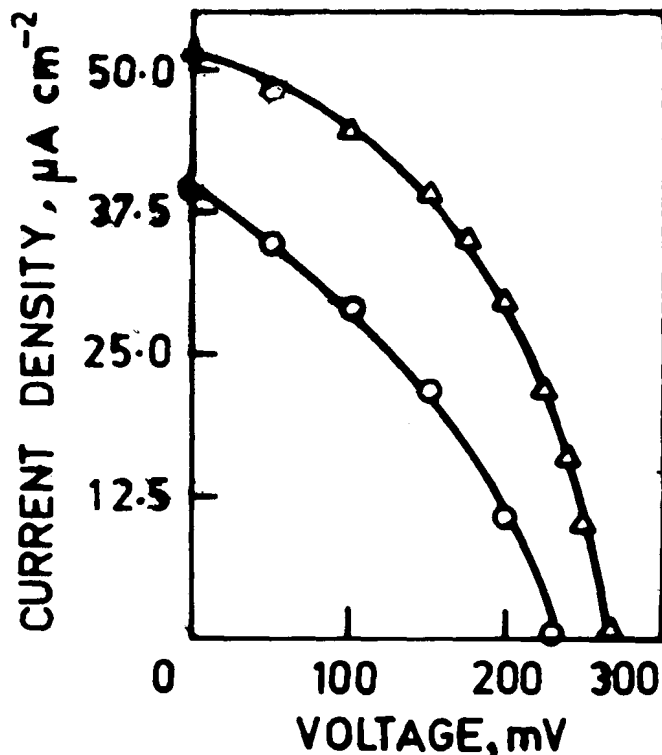


Fig. 3: Current-voltage curves for the cell n-CdS/1M NaOH-1M Na₂S-1M S/Pt at 120 mW cm⁻² illumination; O-chemically etched Δ -photoetched

The absolute quantum efficiency for the different wavelengths is shown in Fig. 4. The wavelength corresponding to the onset of photocurrent is 480 nm. This is in good agreement with the redox transmittance which begins only beyond a wavelength of 480 nm. The photoetched surface shows a maximum quantum efficiency of 2.26×10^{-2} at a wavelength of 510 nm; the chemically etched surface, on the other hand, shows a maximum quantum efficiency of 0.86×10^{-2} at 510 nm. The decrease in the latter case may be due to increased surface recombination on the chemically etched surface. The other features of the quantum efficiency curves are as follows. A large sub-band gap response with a maximum quantum efficiency of 0.96×10^{-2} in the case of the chemically etched electrode and a comparatively lower maximum quantum efficiency of 0.45×10^{-2} in the case of the photoetched electrode are observed. Both the maxima (of Q.E.) occur at exactly the same wavelength of 550 nm. These results show that photoetching results in a reduction of the density of surface states (which are responsible for most of the sub-band gap photocurrent) approximately by two times at 2.25 eV, corresponding to 550 nm. Spectral response cut-offs at 700 nm and 740 nm are observed for photoetched and chemically etched surfaces respectively.

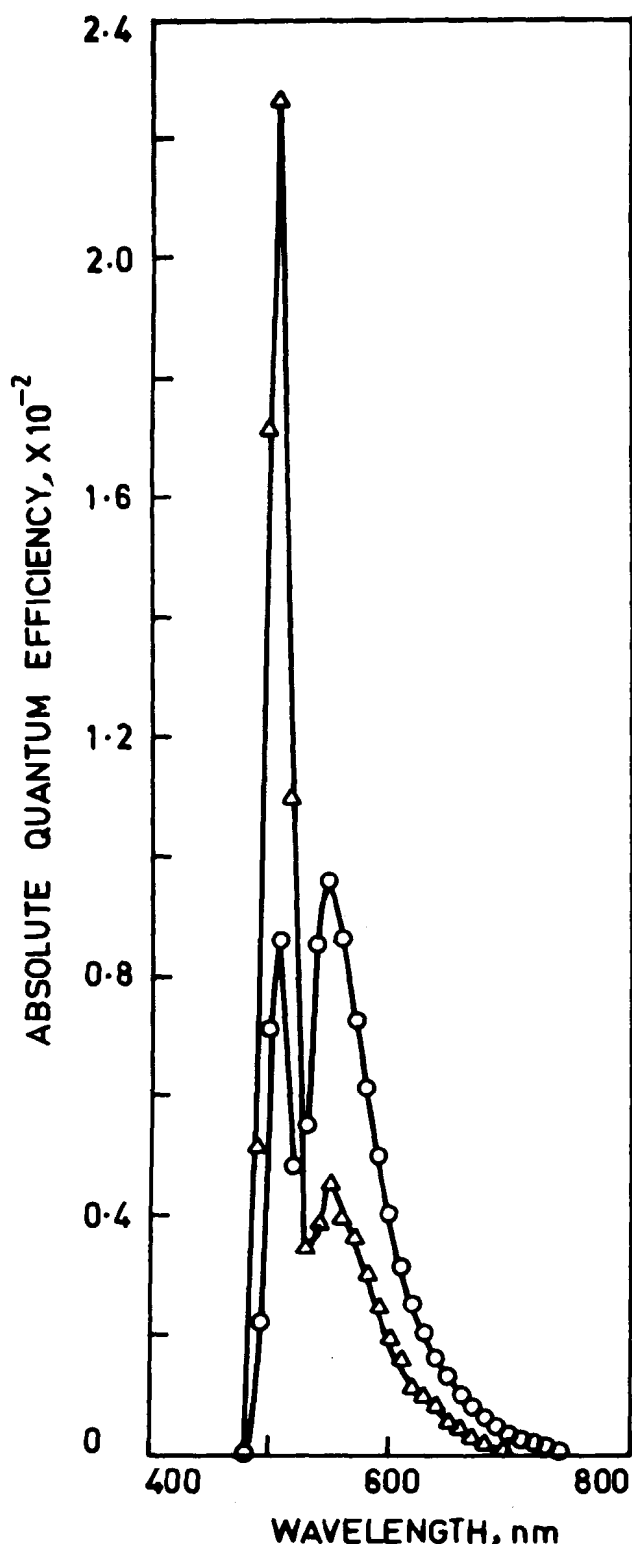


Fig.4: Variation of absolute quantum efficiency for the PEC cell with wavelength of incident radiation; O—chemically etched Δ—photoetched

CONCLUSIONS

Photoetching is a technique to improve the surface of a semiconductor electrode in PEC cells. This has been clearly demonstrated by the higher photo-output characteristic, higher quantum efficiency for supra-band gap illumination and a lower sub-band gap response, in comparison to a chemically etched surface. The improvement can be related to reduced surface defects, reduced reflection losses and increased surface area.

Acknowledgement: The authors wish to thank Dr. V K Venkatesan, Head, Electrochemical Materials Science Division for his encouragement.

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